

Investigations on Passivity of Fe in Borate and Phosphate Buffer, pH 8.4

P. Schmuki, H. Hildebrand, I Wassermann, M. Kolacyak,
I. Kobanenko, *S. Virtanen
University of Erlangen Nuremberg,
Dept. of Materials Science,
LKO, Martensstr. 7, 91058 Erlangen, Germany
*Swiss Federal Institute of Technology, Department of
Materials and
Institute of Materials Chemistry and Corrosion
ETH-Hoenggerberg, 8093 Zurich, Switzerland

In recent years, a growing number of investigations on passivity of Fe and Fe base alloys using modern *in situ* techniques such as synchrotron based X ray absorption near edge structure (XANES) has been carried out [e.g., ref. (1-9)]. The XANES method allows to carry out the experiments *in situ* and hence monitor electrochemical reactions as they are occurring. Using thin film samples, information on the valency of the element studied as well as on eventual dissolution (material loss) can be obtained. Therefore, mechanistic information on electrochemical reactions of passive films has been obtained. This technique, however, suffers from the lack of depth-resolved information, i.e., the information collected represents the average behavior of the whole thin film sample (of the volume the X-ray beam passes). As a result from this, the sensitivity to detect the presence of minor constituents in the surface films is limited.

In the present work, therefore, information collected in previous *in situ* studies is completed by carrying out surface analytical experiments, in order to refine or verify models suggested for the reactions mechanisms of native and artificial passive films. Of a special interest is to further elucidate the influence of solution chemistry on the nature of the passive film on Fe and Fe-Cr alloys, and resulting stability of the films against reductive and oxidative dissolution.

Previous XANES studies on the electrochemical behavior of Fe and thin, sputter-deposited films of Fe₂O₃ in borate buffer (pH 8.4, phosphate buffer (pH 8.4) and in 0.1 M NaOH revealed that the reactions taking place during reduction of the passive film on iron are significantly different for all three electrolytes. In borate buffer (pH 8.4), reduction leads to a complete dissolution of the passive film. In alkaline solution, no dissolution takes place, but, instead, the passive film is converted into a lower-valent oxide/hydroxide film during reduction. Similarly, in phosphate buffer (pH 8.4), there is no dissolution in a direct step to low cathodic potentials, but the resulting reduction product is metallic iron. In an alkaline phosphate-containing solution, conversion into metallic iron, Fe(0), is possible in a direct reduction step to potential in the stability region of Fe(0); at intermediate potentials, a ferrous layer is formed in the reduction reaction. The presence of phosphate species in the electrolyte enables the further reduction of this ferrous layer into Fe(0) at lower potentials. In pure NaOH solution, the presence of Fe(OH)₂ on the surface hinders further reduction even at very low cathodic potentials. The origin and detailed mechanism of the different reduction behavior in the various solutions, however, could not be resolved in the XANES investigations. Direct chemical information on the presence/absence of different electrolyte constituents in the surface films may be able to clarify this question further.

Another topic of interest is the behavior of Fe during active/passive-transition. In contrast to the behavior in alkaline solution, where no dissolution takes place independent of the potential, in the phosphate buffer (pH

8.4), dissolution occurs in the potential range of the active/passive-transition. In this potential region, dissolution is significantly slower in the phosphate buffer as compared with borate buffer. The nature of corrosion films formed on Fe in phosphate-containing solutions has been studied previously - this system has been of a considerable interest, since phosphates are commonly used as corrosion inhibitors for iron (10-14). The results of the previous studies are in good agreement in showing that the films formed in phosphate-containing solutions on Fe contain phosphate-species. The detailed composition of the films, however, depends on passivation conditions, and hence cannot be easily compared with other experiments for instance in borate buffer solution. Therefore, the previous data cannot be directly used to explain the specific role of anions in the behavior of passive iron.

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